

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
21 June 2001 (21.06.2001)

PCT

(10) International Publication Number
WO 01/44312 A1

- (51) International Patent Classification⁷: C08F 4/654, 4/68
- (21) International Application Number: PCT/KR00/01455
- (22) International Filing Date:
13 December 2000 (13.12.2000)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
1999/0057472 14 December 1999 (14.12.1999) KR
- (71) Applicant (*for all designated States except US*): SAM-SUNG GENERAL CHEMICALS, LTD. [KR/KR]; San 222-2, Dokgod-ri, Daesan-up, Seosan-shi 356-874 (KR).
- (72) Inventors; and
- (75) Inventors/Applicants (*for US only*): ROH, Sung-Gun [KR/KR]; Na-405, Samsung Apt., 126-1, Samsung-dong, Kangnam-ku, Seoul 135-090 (KR). CHANG, Ho-Sik [KR/KR]; 109-405, Sejong Apt., Jeonmin-dong, Yuseong-ku, Daejeon 302-728 (KR). HWANG, Gyo-Hyun [KR/KR]; 301-1403, Expo Apt., 464-1, Jeonmin-dong, Yuseong-ku, Daejeon 305-761 (KR).
- (74) Agents: YIM, Suk-Jae et al.; 823-1, Poonglim bldg., Yeoksam-dong, Kangnam-ku, Seoul 135-784 (KR).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:
— With international search report.
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: PREPARATION METHOD OF SUPPORTED CATALYST FOR POLYMERIZATION OF ETHYLENE AND CO-POLYMERIZATION OF ETHYLENE/ALPHA-OLEFIN

(57) Abstract: A preparation method of catalyst for polymerization of ethylene and co-polymerization of ethylene and alpha-olefin is provided. The preparation method of catalyst of the present invention comprises a) producing a carrier by reacting organic magnesium compound of $MgPh_2 \cdot nMgCl_2 \cdot mR_2O$ (wherein Ph=phenyl, $n=0.37\sim0.7$, $m \geq 1$, R_2O =ether) with organic chlorine compound and silicon compound at $-20\sim-80^\circ C$, wherein the molar ratio of the organic chlorine compound to Mg is 0.5 or more, and the molar ratio of the silicon compound to Mg is 0.001 or more; and b) treating said carrier with vanadium compound only or with mixture of vanadium compound and titanium compound.



WO 01/44312 A1

PREPARATION METHOD OF SUPPORTED CATALYST FOR
POLYMERIZATION OF ETHYLENE AND CO-POLYMERIZATION
OF ETHYLENE/ALPHA-OLEFIN

5 Technical Field

The present invention relates to a preparation method of catalyst for polymerization of ethylene and co-polymerization of ethylene and alpha-olefin, and in particular, to a preparation method of supported catalyst containing vanadium compound only
10 or vanadium compound and titanium compound together on a magnesium containing carrier with controlled particle size. The present invention also relates to a ethylene polymerization and copolymerization method using the said catalyst.

15 Background of the invention

The preparation method of supported catalyst for polymerization of ethylene containing transition metal compound on the carrier such as $Mg_mCl_nC_pH_g$ (where $m=0.8\sim0.95$, $n=1.60\sim1.90$, $p=0.8\sim1.6$, $g=1.4\sim3.4$) by using the method of covering transition
20 metal compound on the carrier has been disclosed (US Pat. Nos. 726702, 1400657). Carrier is produced by reacting powder magnesium with alkyl chloride with molar ratio of $RCl/Mg > 2$ using hydrocarbon as a medium.

However, the catalyst produced by the above method has the
25 disadvantage that the particle size of the catalyst powder is widely distributed ($1\sim100\ \mu m$) and is not controlled. And, the polymer powder produced from the catalyst obtained by the above method also has widely distributed size and relatively low bulk density ($0.22\sim0.30 g/cm^3$).

30 It is known that polymerization process can be enhanced by producing polymer with narrow particle size distribution and higher bulk density. For this purpose, catalyst for polymerization with narrow particle size distribution and morphology has been used. In this case, however, catalysts with various average particle sizes

are required since different polymerization method is used for each application. For example, particles with 10~20 μ m are required for slurry polymerization and particles with 25~50 μ m for gas phase polymerization.

5 Catalyst with narrow particle size distribution, including magnesium chloride as a carrier can be obtained by reacting $\text{MgCl}_2 \cdot 3\text{i-C}_8\text{H}_{17}\text{OH}$ compound with TiCl_4 in a hydrocarbon solvent in the presence of electron donor compound such as ethyl benzoate or ethyl anisate(Japanese Patent application No. 59-53511). Catalyst
10 obtained by this method has particle size distribution of 5~15 μ m and high catalytic activity(35Kg-PE/g-Ti, hr, C_2H_4 atmosphere) so that powder polyethylene with narrow particle size distribution and high bulk density can be obtained. But, above method has the disadvantage of requiring very low temperature(down to -20°C),
15 excessive use of TiCl_4 as a reaction medium and generation of much hydrogen chloride during the synthesis. Also above method cannot be used in the production of catalyst with particle size of 15 μ m or more.

One known method of producing catalyst is reacting
20 magnesium-aluminum-alkyl compound($\text{RMgR}_1\text{-nAlR}_2\text{-mD}$) with hydrocarbon chloride, and then reacting obtained solid matter(carrier) with titanium or vanadium halide(German Pat No. 3636060, France Pat. No. 2529207). In this method, (n-Bu)Mg(i-Bu) or (n-Bu)Mg(Oct) dissolved in hydrocarbon is used as an
25 organic magnesium compound, and tert-BuCl is used as a hydrocarbon chloride. Catalyst obtained by this method has the disadvantage that it does not have sufficient catalytic activity.

According to the published European Pat. No. 155,770, the method of producing catalyst by depositing vanadium compounds on
30 the ellipsoidal support of magnesium chloride including product containing electron donor is disclosed. The catalyst is used for preparation of ethylene polymer with wide molecular weight distribution. The above method, however, requires lots of vanadium compounds to fix a little on the support. In the washing process,

lots of vanadium compounds which has not been fixed on the support need to be removed, and it costs high because of the toxicity and corrosiveness of vanadium compounds.

5 Objects of the invention

The object of the present invention is to provide a method of manufacturing polymers with particle size controlled in narrow range, widely distributed molecular weight distribution and high bulk density, and to provide the preparation method of catalyst for
10 polymerization of ethylene and co-polymerization of ethylene and alpha-olefin having high catalytic activity in slurry and gas phase polymerization.

Detailed description of the Preferred Embodiments

15 According to the present invention, the preparation method of catalyst has the characteristic that the carrier obtained by reacting organic magnesium compound $MgPh_2.nMgCl_2.mR_2O$ (wherein Ph=phenyl, $n=0.37\sim0.7$, $m\geq 1$, R_2O =ether) with mixture of organic chlorine compound and silicon compound is treated with active
20 material such as vanadium compound or mixture of vanadium compound and titanium compound.

In the following, the present invention will be described in detail.

According to the preparation method of the present invention,
25 organic magnesium complex agent $[MgPh_2.nMgCl_2.mR_2O]$ which forms a solution with solvent chlorobenzene, ether(R_2O), mixture of chlorobenzene and ether, or mixture of chlorobenzene and aliphatic or aromatic compound is used in the production of magnesium containing carrier. And, suspension of carrier containing solid
30 powder of magnesium is produced by reacting the said solution of organic magnesium compound in a hydrocarbon solvent with organic chlorine compound, preferably carbon tetrachloride and silicon compound, or preferably silicon ethoxide, with the molar ratio of (organic chlorine compound)/Mg ≥ 0.5 and (silicon

compound)/Mg \geq 0.001 at the temperature of $-20 \sim 80^{\circ}\text{C}$. When (organic chlorine compound)/Mg $<$ 0.5, remaining unreacted Grignard reagent(MOC) has undesirable effect on the catalyst, and the limit of (silicon compound)/Mg \geq 0.001 is for obtaining controlled particle size of catalyst. So, by setting (organic chlorine compound)/Mg \geq 0.5, control effect of catalyst particle size can be obtained. Carrier obtained by said method has narrow distribution of particle size and controlled particle size. The size of carrier and catalyst particles are controlled within $5 \sim 100 \mu\text{m}$ by the composition of the organic magnesium compound, molar ratio of silicon compound and organic magnesium compound, and the reaction condition of chlorine compound. The magnesium containing carrier obtained by the said method contains mainly, magnesium dichloride(80~90 weight%), ether(7~18 weight%) and hydrocarbon complex compound(1~5 weight%).

In the present invention, organic magnesium compound used in the production of magnesium containing carrier is produced by reacting powder magnesium with chlorobenzene in the presence of one or more of electron donor, preferably dibutylether or diisoamylether, wherein electron donor can include aliphatic ether and cyclic ether. Aliphatic ether, which has the formula of R_2OR_3 , wherein R_2 or R_3 can be same or different alkyl radical with carbon number of 2~8, is preferably aliphatic ether of carbon number 4~5. Cyclic ether has carbon number 3~5.

For the organic chlorine compound of the present invention, it is preferable to use compound of general formula $\text{CR}'_n\text{Cl}_{(4-n)}$ (wherein n is an integer in the range of 1~3) wherein R' is alkyl radical of carbon number 1~12, and preferable organic chlorine compound is carbon tetra-chloride.

Silicon compound of the present invention has the general formula of $\text{Si}(\text{OR})_a\text{X}_{4-a}$, wherein R stands for aliphatic or aromatic hydrocarbon group with carbon number of 1~14 or COR' (wherein R' is aliphatic or aromatic hydrocarbon group with carbon number of 1~14), X for Cl , Br or I , and a for 0, 1, 2, 3 or 4. Preferably,

silicon compound is silicon alkoxide such as $\text{Si}(\text{OC}_2\text{H}_5)_4$, $\text{Si}(\text{OC}_2\text{H}_5)_2\text{Cl}_2$, $\text{Si}(\text{OC}_2\text{H}_5)\text{Cl}_3$ or $\text{Si}(\text{OC}_2\text{H}_5)_3\text{Cl}$.

Organic chlorine compound and silicon compound can be reacted with organic magnesium compound to produce carrier by one of following five methods. The first method is reacting organic magnesium compound with a mixture of silicon compound and organic chlorine compound. The second method is reacting organic magnesium compound and organic chlorine compound, and after certain time, introducing a solution of mixed silicon compound and organic chlorine compound to react with the organic magnesium compound. The third method is mixing silicon compound and organic magnesium compound, and then organic chlorine compound is introduced to react with the organic magnesium compound. The fourth method is introducing silicone compound after the reaction between organic magnesium compound and organic chlorine compound. And the last method is introducing silicone compound after the titanium or vanadium compound treatment. Among these five methods, the first method is preferred.

The catalyst of the present invention is produced by treating magnesium containing carrier obtained by the above method with one or more of vanadium compound and titanium compound, with the molar ratio of $\text{V/Mg}=0.01\sim 1.0$ and $\text{V/Ti}=0.5\sim 200$ in the hydrocarbon solvent at the temperature of $20\sim 100^\circ\text{C}$. Catalyst produced using vanadium compound and titanium compound of this molar ratio has 1.2 or 2 times higher activity per g-catalyst compared to the catalyst produced using vanadium compound only, and ethylene polymer or co-polymer obtained from this catalyst has wider range of molecular weight distribution compared to the polymer produced using titanium compound only and the inventors of the present invention found that said range can be controlled by the amount of titanium compound used. Also, the catalyst of the present invention is produced by one of the method of supporting titanium compound after supporting vanadium compound on the

carrier, the method of supporting vanadium compound after supporting titanium compound on the carrier, or the method supporting mixture of titanium compound and vanadium compound on the carrier.

5 The vanadium compound used in the present invention has maximum atomic valence of 4 or is a compound with vanadyl(VO) of maximum atomic valence of 3. The vanadium compound has general formula of $V(OR^4)_{4-n}X_n$ or $VO(OR^4)_{3-m}X_m$, wherein R^4 is aliphatic or aromatic hydrocarbon group with carbon number of 1~14 or COR'
 10 (wherein R' is aliphatic or aromatic hydrocarbon group with carbon number of 1~14), X is Cl, Br or I, and a is an integer or fraction between 0~4, and m is an integer or fraction between 0~3. The present invention uses one or more of compound selected from the group of $VaCl_4$, vanadyl trichloride, vanadyl tri-*n*-propoxide,
 15 vanadyl tri-*iso*-propoxide, vanadyl tri-*n*-butoxide, vanadyl tetra-*n*-butoxide and vanadyl tetra-*n*-propoxide.

The titanium compound used in the present invention has general formula of $Ti(OR^4)_aX_b$, wherein R^4 is aliphatic or aromatic hydrocarbon group with carbon number of 1~14 or COR^5 (wherein
 20 R^5 is aliphatic or aromatic hydrocarbon group with carbon number of 1~14), X is Cl, Br or I, and a is an integer between 0~3, and b between 1~4, $a+b$ between 3 and 4. These compounds may be $TiCl_4$, $Ti(OC_3H_5)_4$, $Ti(OC_4H_7)_4$, $Ti(OC_3H_5)_2Cl_2$, $Ti(OC_3H_5)Cl_3$, $Ti(OC_3H_5)_3Cl$, $Ti(OC_4H_7)_2Cl_2$, $Ti(OC_4H_7)Cl_3$ or $Ti(OC_4H_7)_3Cl$.

25 Carrier, if needed, can be treated with organic aluminum compound before being treated with vanadium compound or titanium compound, or before washing after catalyst production with the molar ratio $Al/Ti=0.1\sim2.0$.

The above preparation method of catalyst of the present
 30 invention provides methods for high activity catalyst with narrow particle size distribution and various particle sizes that can be useful for many applications.

According to the present invention, for example, catalyst of particle size $10\sim15\mu m$ which is useful for slurry ethylene

polymerization and catalyst of particle size 20~80 μ m which is useful for gas phase ethylene polymerization can be produced. By using titanium and vanadium as an active component, from polyethylene with narrow molecular weight distribution to
5 polyethylene and polyethylene co-polymer with wide molecular weight distribution can be produced depending on the mixing ratio of titanium and vanadium. Narrow molecular weight distribution may be characterized by melt index ratio of $MI_{21.6}/MI_{2.16} < 30$, and wide molecular weight distribution may be characterized by melt index
10 ratio of $MI_{21.6}/MI_{2.16} > 100$.

The catalyst of the present invention is used in the polymerization of ethylene or co-polymerization of ethylene and alpha-olefin. The catalyst of the present invention can be used as a cocatalyst together with one or more of organic aluminum
15 compound, preferably trialkylaluminum.

Organic aluminum compound which can be used as a cocatalyst has the structural formula of AlR_nX_{3-n} , wherein R is alkyl radical with carbon number of 1~12, X is hydrogen atom, chlorine or halogen molecule such as F, or alkoxy radical with carbon number
20 of 1~12, and n is an integer or fraction between 1~3. For example, triisobutylaluminum, triethyl aluminum, trimethyl aluminum, tri-n-hexyl aluminum, tri-n-octyl aluminum, ethyl aluminum sesquichloride and diethyl aluminum chloride can be used.

Polymerization is carried out by slurry polymerization in the hydrocarbon solvent(such as hexane, heptane) at 50~100 $^{\circ}$ C, or by
25 gas phase polymerization at 60~100 $^{\circ}$ C and 2~40atm without hydrocarbon solvent. As a control agent of molecule of polymer, hydrogen(5~90 volume%) is used. Propylene, butene-1, hexane-1, 4-methylpentene-1, and other alpha-olefin are useful in the
30 polymerization of ethylene alpha-olefin.

In the following, the present invention is described in detail through examples and comparative examples. The following examples, however, are not intended to restrict the scope of the present invention.

Comparative example 1

A. Production of organic magnesium compound

5

In the reactor of 6l with stirrer and temperature controller, 253.6g of magnesium powder(10.44mole) and 3183ml of chlorobenzene(31.32mole) are reacted in the solution of 1799ml of dibutylether(10.44mol) and 37ml of butylchloride as an activator
10 with 2.53g of iodide dissolved. Reaction is carried out in the atmosphere of inert gas(N, Ar) at 80~100°C with stirring, for 10 hours. Then the mixture is maintained for 12 hours without stirring and then liquid phase is isolated from the sediments. Liquid phase is a solution of organic magnesium compound of composition of
15 $\text{MgPh}_2 \cdot 0.5\text{MgCl}_2 \cdot 2(\text{C}_4\text{H}_9)_2\text{O}$ dissolved in the chlorobenzene (with Mg 1.0mole/l).

B. Production of carrier

20

3000ml of the solution(3.0 mole of Mg) obtained by step A is introduced to the reactor equipped with stirrer, and 289ml of CCl_4 (3.0 mole CCl_4) dissolved in the 289ml of heptane is added to the reactor at 60°C over 2 hours. Reacted mixture is stirred for 60 minutes at the same temperature, and then solvent is
25 removed and sediments are washed four times with 2000ml of heptane at 60°C. As a result, powder organic magnesium carrier is obtained suspended in the heptane.

C. Production of catalyst

30

100 g of the carrier obtained is treated with ethyl aluminum chloride solution with the molar ratio of $\text{AlEt}_2\text{Cl}/\text{Mg}=1$ at 4°C for 2 hours, and washed 4 times with 300ml of n-hexane. The production of catalyst is carried out by treating said carrier with VCl_4

solution(with 18.6ml of 0.951mol VCl_4/ml) in the CCl_4 for 1 hour at 60°C. Catalyst is washed with 70ml of n-hexane twice. Catalyst obtained contains 1.2weight% of vanadium and has average particle size of 75 μm .

5 Polymerization of ether is carried out in the steel reactor of 2l with stirrer and temperature control jacket. As a hydrocarbon solvent, n-hexane(1000ml) is used, and as a cocatalyst 2mmol of $\text{Al}(\text{Bu})_3$. Polymerization is carried out at 7.5 atm of ethylene pressure and 910 cc(0°C, 1atm) of hydrogen pressure at 80°C for an
10 hour.

Catalyst corresponding to 0.015mmol of vanadium was taken into this experiment, and 109g of polymer was produced as a result. Catalytic activity is 2.1kg per 1g of catalyst.

Melting index(MI) of polyethylene was 0.125g/10min under
15 2.16kg and 190°C, and the melting index ratio of 21.6kg to 2.16kg was 110. Bulk density of polyethylene powder was 0.36g/cm³, and according to the molecular body analysis data, average particle size of polyethylene powder was 450 μm . Polyethylene powder has narrow particle size distribution. SPAN calculated from molecular
20 body analysis data by the following formula was 0.6.

$\text{SPAN} = (\text{d}_{90} - \text{d}_{10})/\text{d}_{50}$, wherein d_{90} , d_{50} and d_{10} means polyethylene particle size with 90, 50 and 10 weight %, respectively.

25 Example 1

In step B of comparative example 1, 40.5 ml of silicon ethoxide and 289 ml of CCl_4 mixed in 249 ml of n-hexane is used to produce catalyst, instead of using organic magnesium compound and 289 ml of CCl_4 (3.0 mole CCl_4) dissolved in the 289 ml of heptane, other
30 processes being equal as in the comparative example 1.

Example 2

In step B of comparative example 1, 40.5 ml of silicon ethoxide and 289 ml of CCl_4 mixed in 249 ml of n-hexane is used to produce

catalyst instead of using organic magnesium compound and 289 *ml* of CCl_4 (3.0 mole CCl_4) dissolved in the 289 *ml* of heptane, other processes being equal except that the catalyst produced by example 1 is reacted with TiCl_4 and VCl_4 of the molar ratio of
 5 $\text{Ti/V}=0.3$ for an hour and washed with 70*ml* of hexane twice. The physical property and polymerization results are shown in table1.

Example 3

In example 1, 20.2 *ml* of silicon ethoxyde is used, others being
 10 equal as in the example 1. The physical property and polymerization results are shown in table1.

Example 4

Using the catalyst obtained in example 1, co-polymerization of
 15 ethylene and 1-hexene is carried out. The process is the same as example 2 except that 30cc of 1-hexene is used before polymerization. As a result of polymerization, ethylene with density of 0.930g/cc and 1-hexene co-polymer is produced. The results of polymerization are shown in table1.

20

Table1

	Si/ Mg	V (weight%)	Ti (weight%)	Activity	Catalyst Particle size(μ m)	MI2.16	MI21.6/ MI2.16	Bulk density (g/cc)	SPAN ratio
				(Kg-PE)/ (gCat·hr)					
Comparative Example 1	0	1.7	0	2.1	65	0.13	110	0.33	<0.6
Example 1	0.06	1.27	0	1.0	40	0.01	98	0.32	<0.6
Example 2	0.06	1.32	0.3	4.5	40	0.02	82	0.34	<0.6
Example 3	0.03	1.33	0	1.3	53	0.01	105	0.34	<0.6
Example 4	0.03	1.27	0	2.3	40	0.12	128	0.34	<0.6

The effect of the invention

25

As shown above, the preparation method of catalyst of the

present invention provides supported catalyst useful for polymerization of ethylene and co-polymerization of ethylene and alpha-olefin which can produce polyethylene and polyethylene co-polymer with controlled particle size.

Claims

What is claimed is:

1. A method for producing a catalyst for polymerization of ethylene
5 and co-polymerization of ethylene and alpha-olefin, comprising:
 - a) producing a carrier by reacting organic magnesium compound of $\text{MgPh}_2 \cdot n\text{MgCl}_2 \cdot m\text{R}_2\text{O}$ (wherein Ph=phenyl, $n=0.37\sim 0.7$, $m \geq 1$, R_2O =ether) with organic chlorine compound and silicon compound at $-20\sim 80^\circ\text{C}$, wherein the molar ratio of the organic
10 chlorine compound to Mg is 0.5 or more, and the molar ratio of the silicon compound to Mg is 0.001 or more; and
 - b) treating said carrier with vanadium compound only or with mixture of vanadium compound and titanium compound.
- 15 2. The method according to Claim 1, wherein the reaction of the organic magnesium compound with the organic chlorine compound and the silicon compound is performed by reacting organic magnesium compound with a mixture of silicon compound and organic chlorine compound.
- 20 3. The method according to Claim 1, wherein the reaction of the organic magnesium compound with the organic chlorine compound and the silicon compound is performed by reacting the organic magnesium compound and the organic chlorine compound, and after
25 certain time, introducing a solution of mixed silicon compound and organic chlorine compound to react with the organic magnesium compound.
- 30 4. The method according to Claim 1, wherein the reaction of the organic magnesium compound with the organic chlorine compound and the silicon compound is performed by mixing the silicon compound and the organic magnesium compound, and then the organic chlorine compound is introduced to react with the organic magnesium compound.

5. The method according to Claim 1, wherein the reaction of the organic magnesium compound with the organic chlorine compound and the silicon compound is performed by introducing the silicone compound after a reaction of the organic magnesium compound and the organic chlorine compound.

6. A method for producing a catalyst for polymerization of ethylene and co-polymerization of ethylene and alpha-olefin, comprising:

10 a) producing a carrier by reacting organic magnesium compound of $\text{MgPh}_2 \cdot n\text{MgCl}_2 \cdot m\text{R}_2\text{O}$ (wherein Ph=phenyl, $n=0.37\sim 0.7$, $m \geq 1$, R_2O =ether) with organic chlorine compound at $-20\sim 80^\circ\text{C}$, wherein the molar ratio of the organic chlorine compound to Mg is 0.5 or more; and

15 b) treating said carrier with vanadium compound only or with mixture of vanadium compound and titanium compound, and then introducing silicone compound, wherein the molar ratio of silicon compound to Mg is 0.001 or more.

20 7. The method according to any of Claims 1 to 6, wherein said organic magnesium compound is produced by reacting metal magnesium with chlorobenzene in the presence of dibutylether or diisoamylether.

25 8. The method according to any of Claims 1 to 6, wherein said organic chlorine compound has general formula $\text{CR}'_n\text{Cl}_{(4-n)}$ (wherein R' is alkyl radical of carbon number 1~12 and "n" is an integer in the range of 1~3)

30 9. The method according to Claim 8, wherein said organic chlorine compound is carbon tetrachloride.

10. The method according to any of Claims 1 to 6, wherein said silicon compound has the general formula of $\text{Si}(\text{OR})_a\text{X}_{4-a}$, wherein R

is aliphatic or aromatic hydrocarbon group with carbon number 1~14 or COR' (wherein R' is aliphatic or aromatic hydrocarbon group with carbon number of 1~14), X is Cl, Br or I, and "a" is 0, 1, 2, 3 or 4.

5

11. The method according to Claim 10, wherein said silicon compound is silicon alkoxide.

12. The method according to any of Claims 1 to 6, wherein said
10 vanadium compound has general formula of $V(OR^4)_{4-n}X_n$ or $VO(OR^4)_{3-m}X_m$, wherein R^4 is aliphatic or aromatic hydrocarbon group with carbon number of 1~14 or COR_5 (wherein R_5 is aliphatic or aromatic hydrocarbon group with carbon number of 1~14), X is Cl, Br or I, and "n" is an integer or fraction between 0~4, and
15 "m" is an integer or fraction between 0~3.

13. The method according to any of Claims 1 to 6, wherein said titanium compound has general formula of $Ti(OR^4)_aX_b$, wherein R^4 is aliphatic or aromatic hydrocarbon group with carbon number of
20 1~14 or COR^5 (wherein R^5 is aliphatic or aromatic hydrocarbon group with carbon number of 1~14), X is Cl, Br or I, and "a" is an integer between 0~3, and b between 1~4, and a+b is 3 or 4.

14. The method according to any of Claims 1 to 13, wherein said
25 catalyst is produced by one of the method of supporting titanium compound after supporting vanadium compound on the carrier, the method of supporting vanadium compound after supporting titanium compound on the carrier, or the method supporting mixture of titanium compound and vanadium compound on the carrier.

30

15. The method according to any of the Claims 1 to 14, wherein the carrier is additionally treated with organic aluminum compound with the molar ratio of Al/Ti = 0.1~2.0 before or after being treated with vanadium compound or a mixture of vanadium compound and

titanium compound.

16. The method according to any of Claims 1 to 15, wherein the catalyst has the molar ratio of $V/Mg = 0.01 \sim 1.0$ and the molar ratio
5 of $V/Ti = 0.5 \sim 200$.

17. An ethylene polymerization or copolymerization method, wherein the method is performed using the catalyst produced by the method according to any of the Claims 1 to 16 and organic
10 aluminum compound as cocatalyst.

18. The method according to Claim 17, wherein said organic aluminum compound is alkyl aluminum compound of AlR_nX_{3-n} , wherein R stands for alkyl radical with carbon number of 1~12, X
15 for hydrogen atom or halogen atom such as Cl or F, or alkoxy radical with carbon number of 1~12, and "n" for an integer or fraction thereof between 1~3.

19. The method according to Claim 18, wherein said organic
20 aluminum compound is trimethyl aluminum, triethyl aluminum, or trioctyl aluminum.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR00/01455

A. CLASSIFICATION OF SUBJECT MATTER**IPC7 C08F 4/654, C08F 4/68**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7 C08F 4/654, C08F 4/68

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

KOREAN PATENTS AND APPLICATIONS FOR INVENTIONS SINCE 1975

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	KR 97-027116 A (SAMSUNG GENERRAL CHEMICALS AO. LTD.), 24 JUNE 1997(24.06.1997) SEE ABSTRACT AND CLAIM	1 - 8
Y	EP 0767003 A (INSTITUT KATALIZA IMENI G.K. BORESKOVA SIBIRSKOGO OTODELENIA ROSSIISKII NAUK.), 09 APRIL 1997(09.04.1997) SEE ABSTRACT AND CLAIM	1 - 8
A	JP 01115909 A (SUMITOMO CHEMCAL CO., LTD.), 09 MAY 1989(09.05.1989) SEE THE WHOLE DOCUMENT	1 - 19
A	JP 05214025 A (ECP ENICHEM POLIMERI S.R.I.), 24 AUGUST 1993 (24.08.1993) SEE THE WHOLE DOCUMENT	1 - 19
A	EP 0832136 A (QUANTUM CHEMICAL CORPORATION), 01 APRIL 1998 (01.04.1998) SEE THE WHOLE DOCUMENT	1 - 19



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance
 "E" earlier application or patent but published on or after the international filing date
 "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)
 "O" document referring to an oral disclosure, use, exhibition or other means
 "P" document published prior to the international filing date but later than the priority date claimed

"I" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
 "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
 "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
 "&" document member of the same patent family

Date of the actual completion of the international search

12 MARCH 2001 (12.03.2001)

Date of mailing of the international search report

13 MARCH 2001 (13.03.2001)

Name and mailing address of the ISA/KR

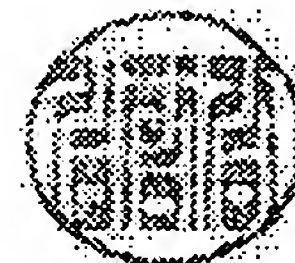
Korean Industrial Property Office
 Government Complex-Taejon, Dunsan-dong, So-ku, Taejon
 Metropolitan City 302-701, Republic of Korea

Facsimile No. 82-42-472-7140

Authorized officer

KIM, Jang Gang

Telephone No. 82-42-481-5544



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR00/01455

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 01115909 A	09.05.1989	EP 0314131 A US 4940682 A CA 1327348 A	03.05.1989 10.07.1990 01.03.1994
JP 05214025 A	24.08.1993	EP 0536840 A US 5320995 A AU 2617192 A CA 2080147 A	12.04.1993 14.06.1994 22.04.1993 10.04.1993
EP 0832136 A	01.04.1998	US 5587439 A WO 9635726 A	24.12.1996 14.11.1996
EP 0767003 A	09.04.1997	JP 09176226 A US 5696044 A WO 9535163 A	08.07.1997 09.12.1997 28.12.1995